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ELECTRONIC COMPUTATIONS OF LIGHT SCATTERING FUNCTIONS  
FOR HETERODISPERSE SYSTEMS OF ISOTROPIC SPHERES

By

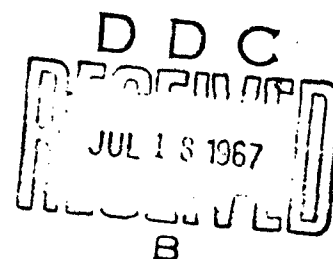
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#### INTRODUCTORY REMARKS

The material given in Technical Report No. 15(61) represented a "Long Abstract" as required by ACS regulation of papers to be presented at a national meeting. Following suggestions made after the meeting at Miami Beach where Dr. Yajnik presented the material, it was decided to make the material available to the general public by publication. This decision, on the other hand, entailed a rewriting of the paper, an appreciable increase in documentary material beyond that originally available and additional checks of the computations made. The resulting considerably revised and enlarged edition which is now being submitted for publication in the J. Polymer Sci., differed sufficiently from Technical Report No. 15(61) that its re-issuance as Technical Report No. 15A(61A) seemed to be warranted.

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ELECTRONIC COMPUTATIONS OF LIGHT SCATTERING FUNCTIONS  
FOR HETERODISPERSE SYSTEMS OF ISOTROPIC SPHERES

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I. INTRODUCTION

An important problem in the characterization of disperse systems, such as polymer lattices, emulsions, etc., is the determination of their particle size distribution. Various experimental techniques have been used for this purpose. Light scattering methods are among the most promising ones. They have the advantage over other methods (e.g. centrifugation, electron microscopy) in that they are relatively simple experimentally, do not affect the state of the systems and are very sensitive to rapid changes in particle size. It is therefore possible, in principle, to obtain "instantaneous" size distributions and to study their variation with time. The advent of computers has greatly enhanced the attractiveness of light scattering methods for the determination of size distribution curves since thereby the formerly very appreciable amount of time required for calculations has been reduced drastically.

The purpose of this paper is to show how the use of a computer can allow one to obtain the size distribution of relatively large spherical particles from light scattering data. We will be concerned specifically with the application of the Mie theory because the systems investigated contained isotropic spherical particles whose refractive index differs appreciably from that of the medium. The computer was used for the solution of two problems: firstly, extensive tables of light scattering functions were prepared for a given type of distribution to be discussed below. Secondly, after the experimental light scattering data had been obtained, the computer was used in order to find the best fit between the experimental data and the tabulated theoretical values. Only the first part of the computer application will be considered here.

II. DEFINITIONS AND HISTORICAL REMARKS

While it is, in principle, possible to compute particle size distributions

without introducing any assumption as to the type of distribution function, this approach is at present not practical. Therefore, it has been assumed<sup>1</sup> that the distribution is, in agreement with most distributions in latices and emulsions, unimodal and positively skewed. The function is

$$\begin{aligned} f(r) &= (r - r_0) \exp\left\{-\left[(r - r_0)/s\right]^3\right\} & r > r_0 \\ &= 0 & r \leq r_0 \end{aligned} \quad (1)$$

Here  $cf(r)dr$  is the number of particles per unit volume with radii between  $r$  and  $r + dr$ ,  $c$  is a normalization factor; and  $s$  and  $r_0$  are the distribution parameters:  $s$  is proportional to the distribution width and  $r_0$  is the radius of the smallest particles present in statistically significant numbers. It is advantageous to introduce dimensionless parameters

$$p = \frac{2\pi r_0}{\lambda} \quad q = \frac{2\pi s}{\lambda} \quad \alpha = \frac{2\pi r}{\lambda} \quad (2)$$

where  $\lambda$  is the wavelength of the incident light in the medium.

There are several light scattering functions which can be used in the evaluation of particle size distributions.

The two methods developed previously in this laboratory involved the determination of the spectra of turbidity and of the spectra of the scattering ratio at an angle of observation of  $90^\circ$ . The scattering ratio  $\sigma = I_{\parallel}/I_{\perp}$ , where  $I_{\parallel}$  and  $I_{\perp}$  are the total intensities of light scattered from an incident linearly polarized beam of unit intensity with the electric vector vibrating in the plane of observation and perpendicularly to the plane of observation respectively. We shall consider here the scattering ratio for a series of angles of observation including  $90^\circ$ . Consequently, the variation of  $\sigma$  with the angle of observation can be used as the third criterion in the determination of particle size distributions\*.

Finally, as a fourth potentially useful argument, the angular variation of  $I_{\parallel}$  and  $I_{\perp}$ , themselves, shall be considered.

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\*Closely related to this is the use of the angular variation of the polarization ratio evaluated by Kerker et al.<sup>2</sup> for certain relatively large refractive index ratios applicable to aerosols.

Considering a system containing optically homogeneous, non-absorbing spheres with a distribution in size  $f(r)$ , the quantities enumerated are, on using the Mie-equations<sup>3</sup>, defined as follows:

$$I_{\parallel} = \frac{\lambda^2 c}{4\pi^2} \int_{r_0}^{\infty} i_{\parallel}(\alpha, \gamma, m) \cdot f(r) dr \quad (3a)$$

$$I_{\perp} = \frac{\lambda^2 c}{4\pi^2} \int_{r_0}^{\infty} i_{\perp}(\alpha, \gamma, m) \cdot f(r) dr \quad (3b)$$

and

$$\sigma = \frac{\int_{r_0}^{\infty} i_{\parallel}(\alpha, \gamma, m) \cdot f(r) dr}{\int_{r_0}^{\infty} i_{\perp}(\alpha, \gamma, m) \cdot f(r) dr} \quad (3c)$$

Making use of equations (2) we get the following expression for the scattering ratio:

$$\sigma = \frac{\int_p^{\infty} i_{\parallel}(\alpha, \gamma, m) \cdot (\alpha - p) \exp\{-[(\alpha - p)/q]^3\} d\alpha}{\int_p^{\infty} i_{\perp}(\alpha, \gamma, m) \cdot (\alpha - p) \exp\{-[(\alpha - p)/q]^3\} d\alpha} \quad (4)$$

The quantities  $i_{\parallel}(\alpha, \gamma, m)$  and  $i_{\perp}(\alpha, \gamma, m)$  in equations (3) and (4) are the basic Mie functions for angular scattering. They depend on  $\alpha$ , on the refractive index of the spheres relative to that of the medium,  $m$ , and on the angle of observation  $\gamma$ , measured with respect to the reverse direction of the incident beam. They are defined as follows

$$i_{\parallel} = \left| \sum_{n=1}^{\infty} [A_n \tau_n(\cos \gamma) + B_n \pi_n(\cos \gamma)] \right|^2 \quad (5a)$$

$$i_{\perp} = \left| \sum_{n=1}^{\infty} [A_n \pi_n(\cos \gamma) + B_n \tau_n(\cos \gamma)] \right|^2 \quad (5b)$$

where

$$A_n = (-1)^n i \frac{2n+1}{n(n+1)} \frac{S_n(\alpha) S_n'(\beta) - m S_n'(\alpha) S_n(\beta)}{\phi_n(\alpha) S_n'(\beta) - m \phi_n'(\alpha) S_n(\beta)}$$

$$B_n = (-1)^n i \frac{2n+1}{n(n+1)} \frac{S_n'(\alpha) S_n(\beta) - m S_n(\alpha) S_n'(\beta)}{\phi_n'(\alpha) S_n(\beta) - m \phi_n(\alpha) S_n'(\beta)}$$

$$i = \sqrt{-1}$$

$$\beta = m\alpha$$

$S_n$  are the Riccati-Bessel functions,  $\phi_n$  are complex functions related to the Hankel functions,  $\pi_n$  and  $\tau_n$  are related to the associated Legendre polynomials. Fuller description of the quantities which enter in the Mie equations has been given elsewhere<sup>4</sup>.

The first systematic attempt to compute solutions of the Mie equations (5a) and (5b) for specific values of the parameters  $\alpha$ ,  $\gamma$  and  $m$  and for monodisperse systems by Blumer, in 1925 had to make use of manual computations.<sup>5</sup> The most recent results obtained by manual computations dealing again with monodisperse systems, were those by Pangonis.<sup>6</sup> They were calculated with a conventional desk calculator. Since it is necessary to take at least  $\alpha$  terms and, preferably,  $(1.43 \alpha + 5)$  terms into the summations defined in equations (5) the practically possible scope of computations was severely limited, however, unless an unreasonably large amount of time was to be devoted to the task. Thus, the computations by Pangonis referred to above, required the better part of one year. Only since the advent and more general availability of electronic computers has it become possible to evaluate the Mie scattering functions without major restrictions in parameter values.<sup>4,6,7</sup> The need for computations by an electronic computer became even more imperative on using the Mie theory for the determination of distribution functions. Here manual computations are virtually impossible because of the prohibitive time required. Stevenson and Heller<sup>8</sup> in a first attempt in this direction have published electronically obtained scattering functions for heterodisperse

systems for  $\sigma$ -values at the single angle  $\gamma = 90^\circ$ .

### III. THE PROGRAMMING TECHNIQUE AND PERFORMANCE CHECKS

The program as developed for the present purpose was written mostly in Fortran for the IBM 7074 computer and consists of several parts. They are concerned with (1) the generation of Bessel functions and Legendre polynomials (2) the evaluation of Mie functions defined by equations (5), and (3) with their integration for specific  $p$  and  $q$  values. The generation of the Riccati-Bessel functions was carried out by downward recursion since this has been found to be more accurate for higher orders.<sup>9</sup> In this connection the method based on the expression of ratios of Bessel functions in terms of continued fractions has been used.<sup>10</sup>

On carrying out the integration for a given pair of  $p$  and  $q$  values, it was of course, necessary to cut off the process of integration at that  $\alpha$  value above which the asymptotically decreasing contribution of higher  $\alpha$ -values to the total scattering is negligible. It was found that the desired accuracy of the scattering function (three figures) was not affected if the cut-off was made at that  $\alpha$ -value at which the value of the distribution function  $f(\alpha)$  has decreased to less than  $10^{-5}$ .

One of the major problems to be resolved was the choice of the best method of integration. For this purpose extensive experimentation was undertaken by means of the computer, the objective being to obtain a sufficiently accurate result without having to use an inordinate amount of machine time. Two classes of methods were used: (1) The Newton-Cotes formulae, and (2) The Gaussian Quadrature. Since the former are equal-interval formulae they are simpler to use, particularly if the values of the integrand are already available. This is due to the fact that one set of data can be used for all integrations (for any  $p$  and  $q$  values). For preliminary checks, some manual computations were performed using both the trapezoidal and Simpson's rule. Both performed satisfactorily. Simpson's rule was considered as preferable however, and adopted because of the oscillatory character of the functions at large  $\alpha$ -values.<sup>11</sup>

It is true that, in principle, the Gaussian Quadrature should give more reliable results if the number of intervals between the integration limits of

the independent variable is made sufficiently large. Therefore, this alternate method, was investigated also more closely. The process of integration was allowed to continue automatically for smaller and smaller subdivisions until the difference between two successive results was less than  $10^{-3}$ . The general procedure is schematically shown in Figure 1, which was prepared with a program using the autochart programming system.\* Unfortunately, the iterations and the necessity of evaluating the Mie functions in each instance took up a major amount of computer time. Therefore, this method is used at the present time for spot-checks only.

A comparison of the results obtained with the two methods of integration is given in Table I, where the bracketed data are taken from Reference 8; in view of the fact that the computing techniques improved in the meantime, the agreement with the present values is satisfactory. It is apparent that a decrease in the  $\Delta x$ -interval from 0.2 to 0.1 does not materially change the result obtained with Simpson's rule, while a decrease is observed in the results obtained with the Gaussian method on changing from 5-node to 9-node computations.\*\*

A comprehensive survey of the performance of the Gaussian Quadrature is given in Figure 2 where the number of nodes is the independent variable and the number of panels is the parameter.

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\* The flow chart given in Figure 1 illustrates in principle also the computing procedure on using Simpson's method except that the absence of nodes eliminates the respective part of the process. In addition, changing intervals between successive  $\alpha$  values is here much simpler.

\*\* The number of nodes define the fixed number of intervals into which each panel is subdivided. A panel, on the other hand, defines one of the  $N$  parts into which the total interval of integration is originally divided. After the first computations the number of panels is increased automatically to  $2N$ ,  $4N$ , etc., the number of nodes being in each instance constant. The machine was programmed to increase the number of nodes systematically after each such operation.



It is apparent that it is necessary at a given  $p$  and  $q$ -value, to have a product of at least 60 for the number of panels and number of nodes in order to obtain a result which does not change further on increase of panels or nodes. It is now interesting to note that the nearly asymptotic value obtained on using a sufficiently large number for the product of nodes and panels is close to the result obtained on using Simpson's rule provided the number of intervals in the latter instance is close to 100. The respective asymptotic values differ by somewhat less than 1.5%.

The satisfactory convergence of the results obtained by the two methods (Simpson's rule and Gaussian Quadrature) on meeting the proper requirements with regard to the number of intervals, and products of panels and nodes, respectively, represented, in principle, sufficient proof for the reliability of the results obtained. Nevertheless still another proof was carried out. It was based on the fact that the scattering ratios considered as a function of  $q$  should extrapolate convincingly, at  $q = 0$ , to the data reported previously for monodisperse systems.<sup>4</sup> That this applies in fact, is illustrated in Figures 3-5. In order to make the extrapolations to  $q = 0$  as secure as possible the interval of integration had to be reduced from  $\Delta\alpha = 0.1$  to 0.01.

The computation of the  $\bar{\sigma}$  values is the second step in the overall computation procedure, the first step being the evaluation of the quantities  $I_{||}$  and  $I_{\perp}$  given in Equations (3a) and (3b). Essentially, all statements made with regard to the computation of  $\bar{\sigma}$  apply also to the computation of these quantities. Figure 6 shows on the example of  $I_{||}$  that it also extrapolates very well to  $q = 0$ . The values pertinent to  $q = 0$  are taken from the book by Denman, Meller, Pangonis<sup>4</sup>.

#### IV. PRELIMINARY DISCUSSION OF THE RESULTS OBTAINED.

It is not intended here to discuss the results proper, their characteristic features and practical application. This will be done in a separate article to be published elsewhere. However, a few salient features may be referred to here. First of all, it is of interest to consider briefly the character of the  $\bar{\sigma}$  vs.  $q$  curves given in Figures 3-5. The curves pertinent to large  $\gamma$ -values ( $\gamma = 90^\circ$  and  $150^\circ$ ) in Figure 3 are quite simple; this is easy to understand since minima and maxima of  $\bar{\sigma}$  enter the forward direction

( $\gamma > 90^\circ$ ) only at rather high  $\alpha$  values.<sup>12</sup> Therefore, an increase in heterodispersity simply increases the  $\bar{S}$ -values monotonically at these large angles of observation. Similarly, the curves are bound to be monotonic at low  $p$  values if  $\gamma < 90^\circ$  as long as  $q$  is reasonably small, the reason being again the absence of minima and maxima. This is apparent from Figure 4 which applies to  $\gamma = 30^\circ$ . However, at larger  $p$ -values for the same  $\gamma$ ,  $\bar{S}$  passes through a minimum or a maximum within the same range of relatively small  $q$ -values. This follows from Figure 5. It is finally, of interest to point out the most characteristic feature of the angular scattering functions derived for heterodisperse systems: Figure 7 shows for  $p = 1.0$  that even a very modest degree of heterodispersion characterized by  $q = 0.1$  increases the numerical value of  $\bar{S}$  at  $90^\circ$  by more than 50%. The increase is about 100-fold at  $q = 1.0$ . In addition, there is an  $8^\circ$  shift in the location of the minimum value of  $\bar{S}$  in the latter instance. It follows from this comparison that the analysis of the size distribution curves will be particularly attractive at those angles where  $\bar{S}$ -minima or maxima occur, because even slight degrees of heterodispersion manifest themselves very clearly.

#### SUMMARY

Fortran programs were developed to compute light scattering functions for heterodisperse systems which can be described by a bi-parametric, unimodal, exponential distribution function. The programs had to include the evaluation of the Mie functions for angular scattering for any arbitrary values of the size parameter  $\alpha$  within the range  $0 < \alpha \leq 25$ . This involved the generation of the Riccati-Bessel functions and Legendre polynomials. Two methods of numerical integration (viz. Gaussian Quadrature and Simpson's rule) of the expressions containing the products of the Mie functions and the distribution function were investigated, and the results were compared. The theoretical results were also checked by extrapolation to the condition of monodispersity characterized by  $q \rightarrow 0$ .

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## LEGENDS

### Figure 1

#### SCHEMATIC DIAGRAM OF THE PROCEDURE OF COMPUTATIONS

The symbols  $m$ ,  $\gamma$  and  $\alpha$  of the text are replaced here by  $M$ ,  $G$  and  $A$  due to technical requirements of the IBM 1403 printer used. Block 08, labelled GROUP, stands for a group of subprograms for the functions indicated.

### Figure 2

#### VARIATION OF COMPUTED $\delta$ -VALUES WITH THE NUMBER OF NODES ON USING THE GAUSSIAN QUADRATURE METHOD

The number of panels is indicated as the parameter.  
 $m = 1.20$ ,  $\gamma = 90^\circ$ ,  $p = q = 4.0$ . The curve was traced from an original plotted by the Calcomp digital curve-plotter with a separate program written for the purpose.

### Figure 3

#### VARIATION OF $\delta$ WITH $q$

$$\gamma = 90^\circ \text{ and } 150^\circ$$

$$m = 1.20. \text{ Parameter } p$$

### Figure 4

#### VARIATION OF $\delta$ WITH $q$ . I. LOW $p$ -VALUES

$$\gamma = 30^\circ$$

$$m = 1.20. \text{ Parameter } p$$

### Figure 5

#### VARIATION OF $\delta$ WITH $q$ . II. INTERMEDIATE $p$ -VALUES

Same details as in Figure 4.

### Figure 6

#### VARIATION OF $L_1$ WITH $q$

$$\gamma = 30^\circ$$

$$m = 1.20. \text{ Parameter } p$$

### Figure 7

#### VARIATION OF $\delta$ WITH $\gamma$ FOR SMALL DEGREES OF HETERODISPERSION ( $\alpha \leq 1.0$ ) AND $p = 1.0$

$$m = 1.20$$

TABLE I  
VALUES COMPUTED BY (A) GAUSSIAN QUADRATURE AND (B) SIMPSON'S RULE  
 $m = 1.20, \gamma = 90^\circ$

q	P	A <sub>1</sub>	A <sub>2</sub>	B <sub>1</sub>	B <sub>2</sub>	B <sub>3</sub>
0.4	0	.00003			.00003	.0000
0.4	4	.31614			.31613	.3028
2.0	0	.10061	.10107	.10013	.10013	.0997
2.0	4	.41845	.41847	.41843	.41846	.4182
4.0	0	.30938	.31223	.30720	.30720	.3049
4.0	4	.56547	.56547	.57309	.57309	.5710

A<sub>1</sub> : 9 nodes

A<sub>2</sub> : 5 nodes

B<sub>1</sub> :  $\Delta\alpha = 0.2$

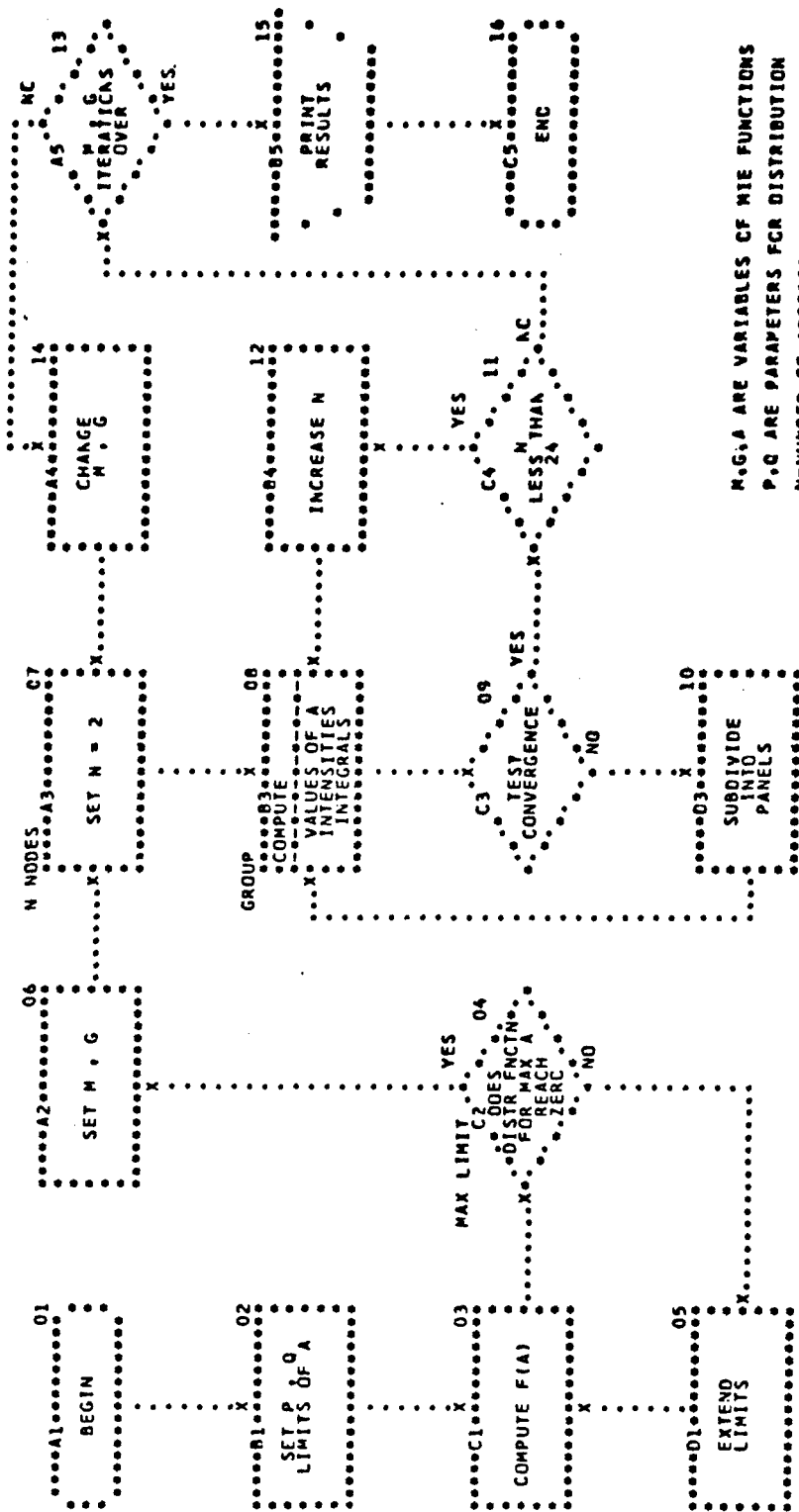
B<sub>2</sub> :  $\Delta\alpha = 0.1$

B<sub>3</sub> : Data from Ref. 8 (computed with  
Simpson's rule,  
 $\Delta\alpha = 0.2$ )

# FIGURE I

CHART A1 AUTOCHART GAUSSIAN QUADRATURE MURUL VAJNIR MAR67

## LIGHT SCATTERING HETERODISPERSE SYSTEMS



M, G, A ARE VARIABLES OF MIE FUNCTIONS  
P, Q ARE PARAMETERS FOR DISTRIBUTION  
N=NUMBER OF ABSCISSAS AND WEIGHTS

FIGURE 2

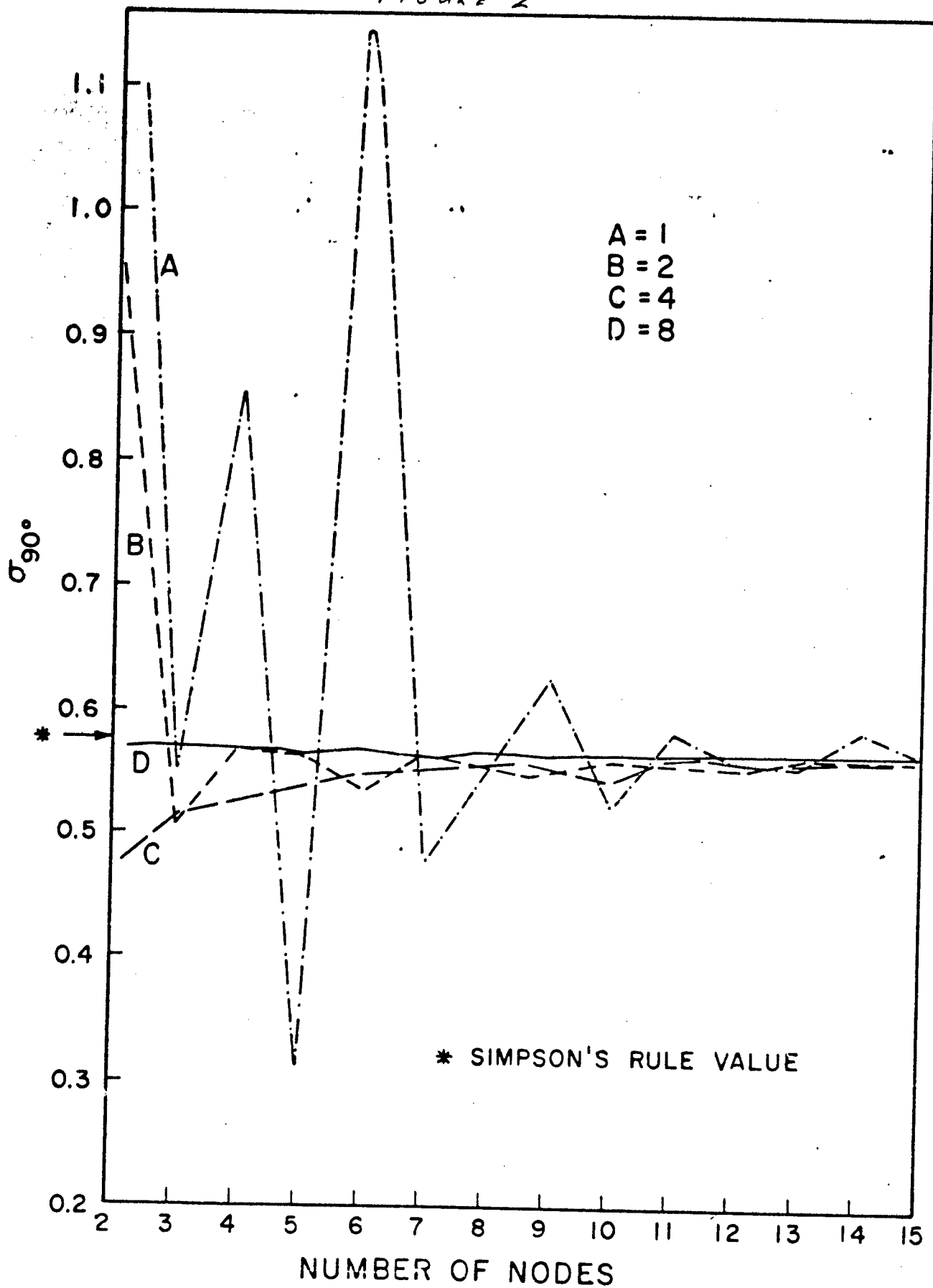


FIGURE 3

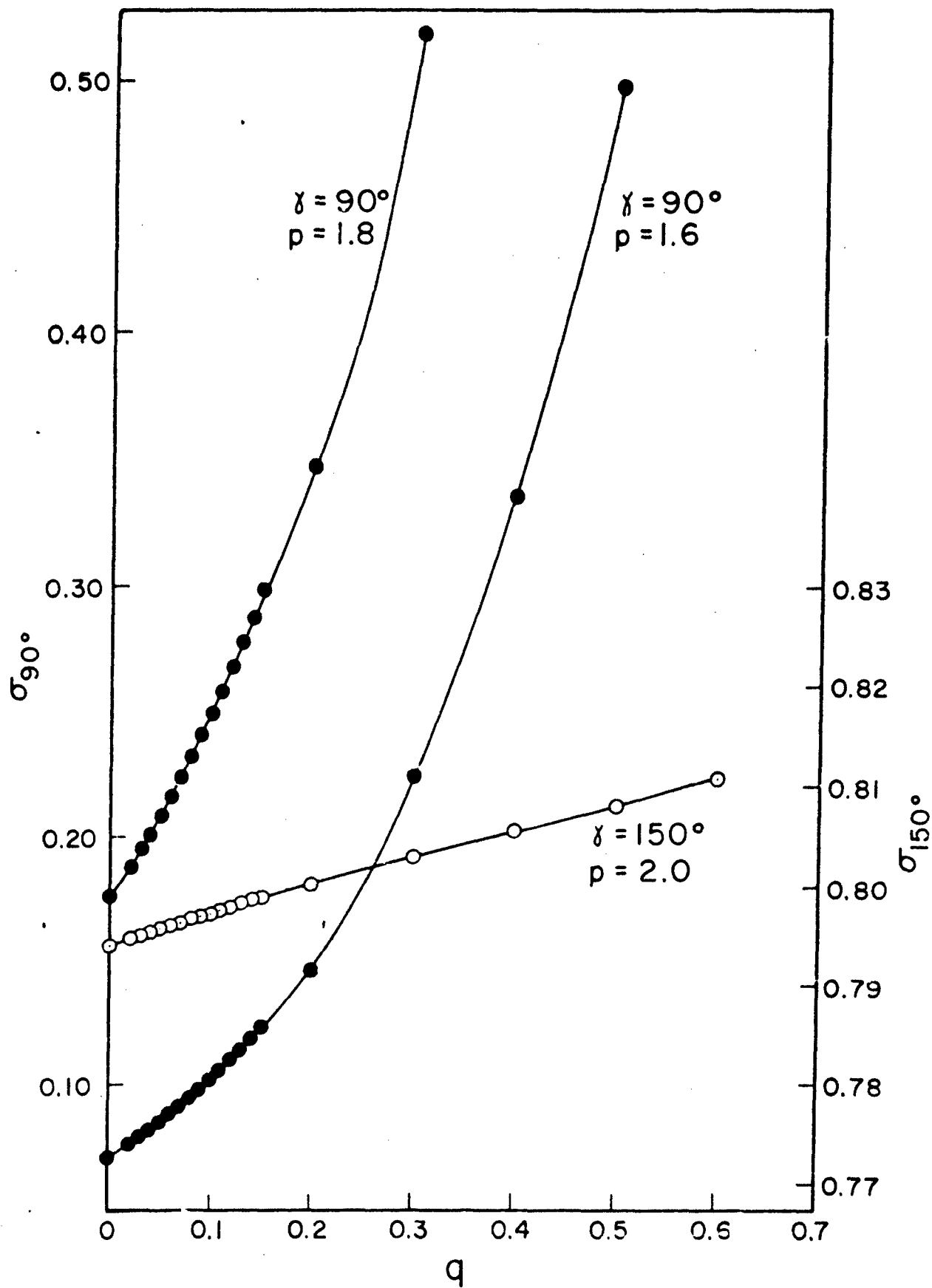




FIGURE 4

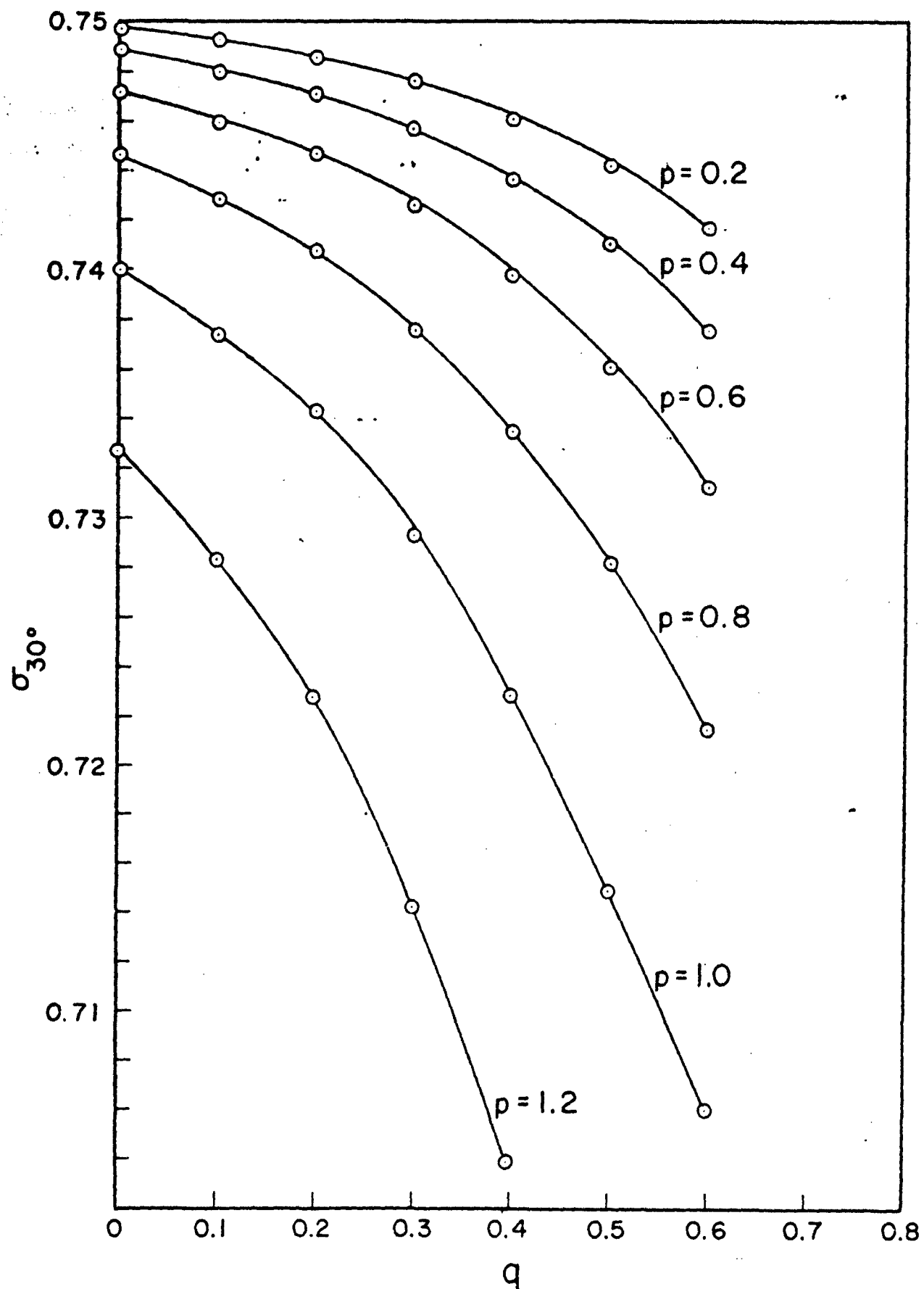


FIGURE 5

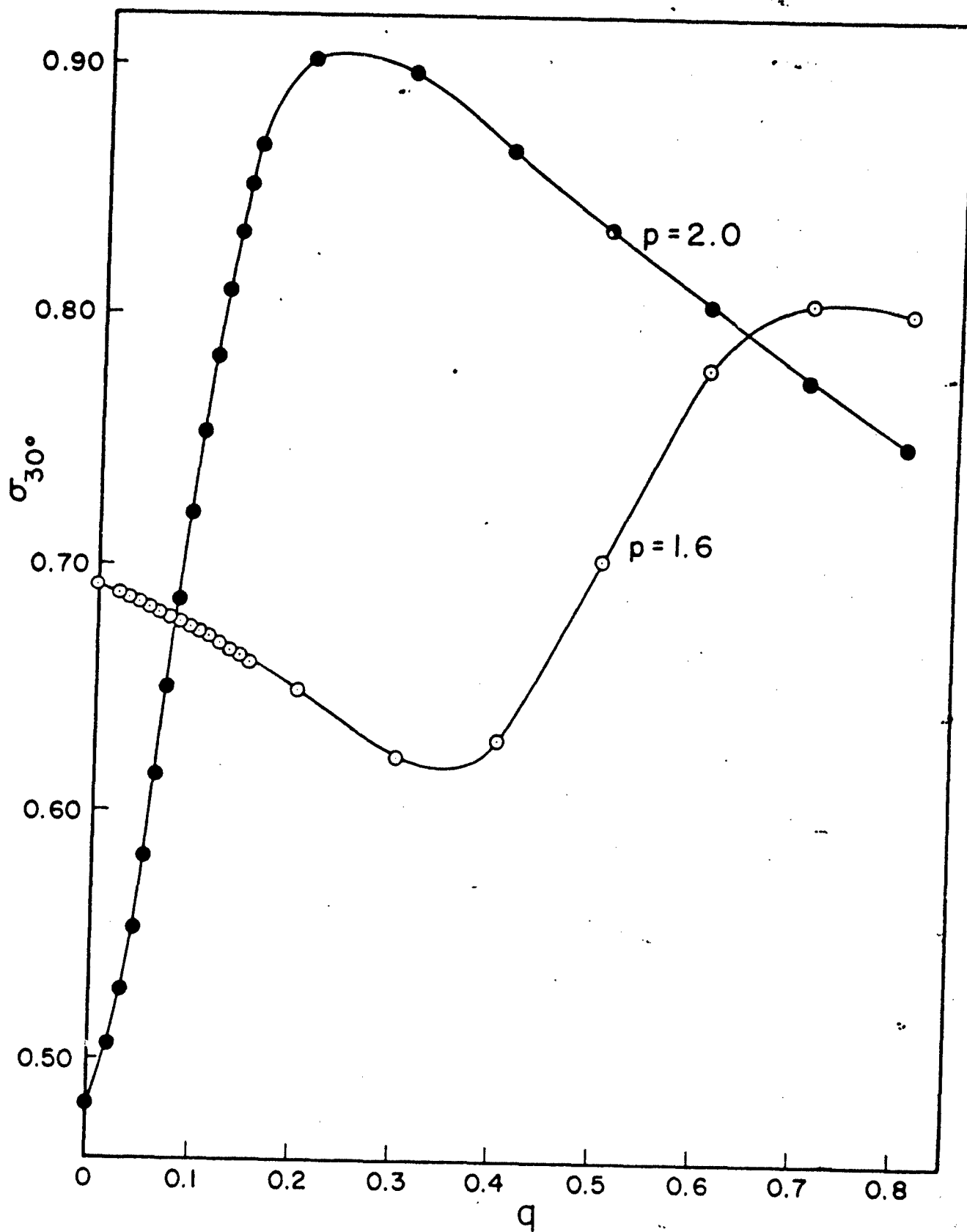


FIGURE 6

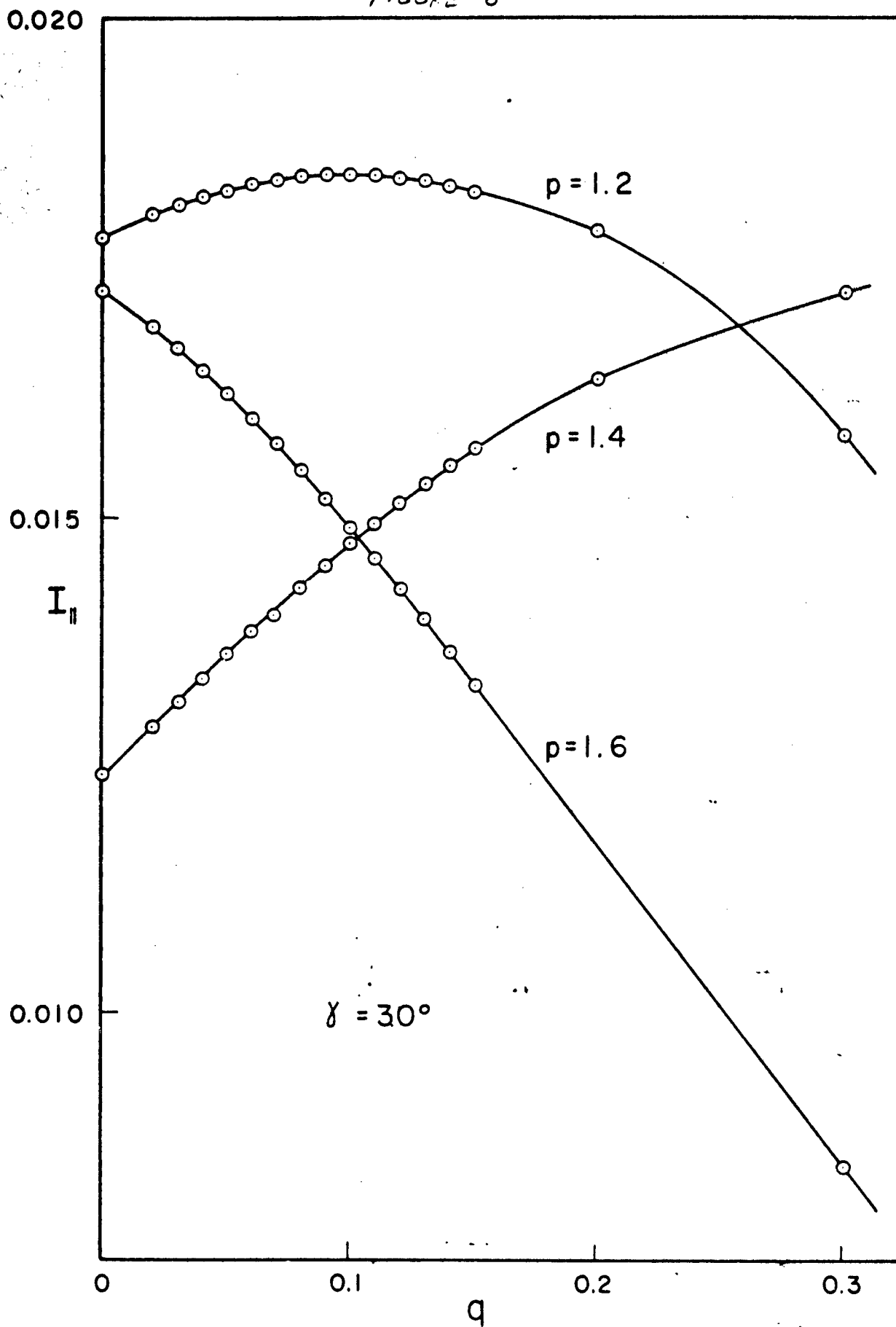
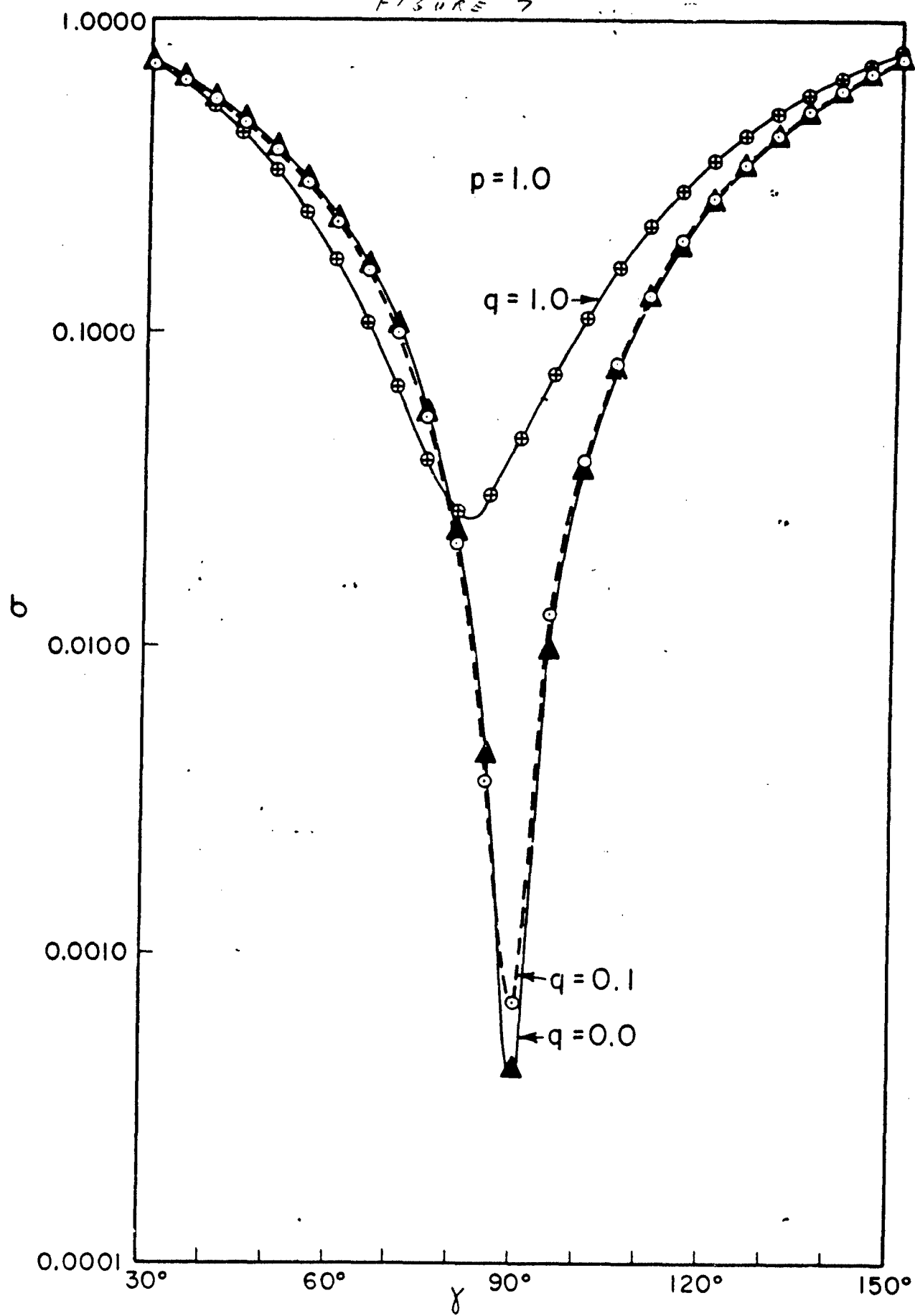


FIGURE 7



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